

COOLSIDE DESULFURIZATION REACTIONS AND MECHANISMS

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ABSTRACT

Coolside desulfurization is an emerging SO_2 control technology, involving injection of a dry sorbent such as hydrated lime and flue gas humidification by water spraying, downstream of the air preheater in a coal-fired boiler unit. The sorbent entrained in the flue gas removes SO_2 in the humidification zone. It also removes SO_2 in the particulate layer collected by the ESP or baghouse. Based on pilot-scale data, the desulfurization mechanism in the humidifier is highly complex. Hydrated lime entrained in the flue gas rapidly reacts with SO_2 at high relative humidity conditions but, in the absence of liquid water, the reaction utilizes only a small fraction of the sorbent. The presence of water droplets in the humidifier significantly increases the sorbent efficiency and the SO_2 removal level by making the sorbent- SO_2 reaction more effective. Increasing the water droplet size also increases the SO_2 removal in the humidifier.

This paper discusses the results of pilot tests which studied the mechanisms of SO_2 capture by hydrated lime in the presence and absence of water droplets in the flue gas.

INTRODUCTION

Coolside desulfurization involves injection of a dry sorbent (typically hydrated lime) followed by flue gas humidification with liquid water sprays in the ductwork downstream of the air preheater in a coal-fired boiler. SO_2 is removed by the entrained sorbent particles in the humidification zone and by the sorbent bed in the particulate collector. Since sorbent residence time in the humidifier is very short (typically 1-3 seconds), a highly active sorbent is needed for a significant humidifier SO_2 removal. Water-soluble additives can be injected with the humidification water to enhance the sorbent activity.

The concept of Coolside technology was successfully demonstrated by Consolidation Coal Company (Consol) in 1 MW field tests at Martinsville, Virginia, in 1984 (1,2). In the field tests, SO_2 removals up to 75-80% were achieved across a pilot humidifier and ESP at sorbent utilizations ranging up to 35-40%, using commercial hydrated lime with NaOH as the additive. The field results indicate that the presence of liquid water droplets plays a key role for high humidifier SO_2 removal. The sorbent activities in the field tests were significantly higher than those observed in laboratory differential reactor tests under humid flue gas conditions without evaporating water droplets (1).

To improve the process performance through process optimization and improved sorbent development, Consol constructed a 0.15 MW pilot test unit (3). A first series of process variable tests made in the pilot unit (3) confirmed the consistency of the pilot SO_2 removal data with the removals observed in the 1 MW field tests.

This paper describes the results of a subsequent pilot research program, which studied the SO_2 removal mechanisms in the humidifier. Two types of tests were conducted:

- Tests with steam humidification, to study sorbent-SO₂ reactions at close approach to adiabatic saturation and short contact times, but in the absence of water droplets.
- Tests with water spray humidification downstream of the lime injection (Coolside humidification), with varying nozzle atomizing conditions to produce different droplet sizes and drying times.

TEST METHODS

The tests of humidifier SO₂ removal mechanisms were made using the 0.15 MW Coolside pilot unit. Both the steam humidification tests and the water spray humidification tests were conducted in this unit.

Pilot Unit

Figure 1 shows a schematic of the pilot unit. The unit consists of a flue gas generation system, Coolside process system (including lime injector and humidifier), a baghouse, and continuous flue gas sampling and analysis systems. The flue gas leaving the baghouse is recycled after removal of excess moisture by a condenser/separator, providing about 80% of the flue gas requirement. The recycle gas is mixed with the flue gas introduced from a natural gas burner. By injecting CO₂, H₂O, SO₂ and fly ash into this combined gas, the inlet flue gas conditions can be matched to the flue gas conditions downstream of the air preheater in a coal-fired boiler. The fly ash content was about 4 grains/scf flue gas and the SO₂ content was 1500 ppm in the tests reported here. The pilot humidifier is a vertical, 8.3-inch ID, cylindrical duct and provides a 20-foot down-flow humidification zone. The flue gas velocity is variable from 8 to 25 ft/sec, giving 0.8-2.5 sec residence times. The humidifier has thermocouples and observation ports every two feet along its length. Hydrated lime (Table 1) is injected into the flue gas at the top of the humidifier. A series of distribution plates is placed between the lime injector and the spray nozzle locations to provide solids mixing and uniform gas flow. In all the tests with water spraying, commercial two-fluid (air/H₂O) nozzles were used. The nozzle water flow controls the humidifier exit gas temperature for the desired approach to saturation. A water soluble additive such as NaOH can be fed as an aqueous solution into the humidification water stream.

The pilot baghouse has a total cloth area of 115 ft², giving a maximum air/cloth ratio of 4.1 acfm/ft² at 150°F.

The pilot unit is installed with two continuous SO₂/O₂ flue gas analysis systems to measure the process SO₂ removal. The O₂ analyses are used to correct for air in-leakage. The SO₂ removal can be measured across the humidifier only or across the humidifier and baghouse. The humidifier exit gas sampling system was specially designed to prevent further SO₂ reaction with reactive solids in the sample system.

Steam Humidification Tests

In the steam humidification tests, a low-temperature (<180°F) gas stream was produced by running the combustor at very low load and operating with a high recycle. The gas was then humidified with steam upstream of the hydrated lime injection point. The humidifier inlet flue gas in the steam humidification tests was equivalent to the flue gas after complete droplet evaporation with water spray humidification. Since the flue gas was free of water droplets, the tests measured SO₂ removal in a dry but humidified environment. Experimental variables were approach to saturation (10-60°F), and Ca/S molar ratio (1-2).

Water Spray Humidification Tests

In the water spray humidification tests, a high-temperature (ca. 300°F) simulated flue gas was humidified to a close approach to adiabatic saturation (20-25°F) by spraying liquid water in the humidifier downstream of the lime injection point. Therefore, liquid water droplets were present with the entrained sorbent until they evaporated completely. In these tests, three different atomizing nozzles were tested, each under widely varying atomizing air pressures/flows. The varying degrees of atomization yielded sprays with widely varying droplet size distributions and drying times (0.7-2.1 sec at 30°F approach). Other experimental variables were approach (20-60°F), Ca/S (1 to 2 by mol) and NaOH/Ca(OH)₂ additive ratio (0 to 0.1 by mass).

RESULTS AND DISCUSSION

Reactivity of Entrained Lime Particles in Humidified Flue Gas

Tests with steam humidification (Figure 2) revealed that entrained hydrated lime particles have a substantial activity for SO₂ capture under humidified flue gas conditions (at low approach to saturation without the presence of liquid water droplets). At 25°F approach to saturation, 2 Ca/S molar ratio and 2 second contact time, the SO₂ removal was 23%. This level of SO₂ removal in the short contact time shows that hydrated lime particles have a high intrinsic activity under the humidified conditions, even in the absence of water droplets. This result indicates that a significant SO₂ reduction is possible in the humidifier by lime which is not directly wetted by water droplets. It also indicates that the lime can continue to capture a significant amount of SO₂ even after complete evaporation of water sprays.

The activity of entrained lime particles under humidified conditions increased significantly with increasing relative humidity (Figure 2). The SO₂ removal at 2 Ca/S mole ratio increased from 12% to 40% as the approach to adiabatic saturation (ca. 125°F) decreased from 60°F (about 20% relative humidity) to 10°F (about 75% relative humidity). At 1 Ca/S ratio, the SO₂ removal increased from 7% to 20% with the same change in the approach.

At higher approaches, the SO₂ removal was not as sensitive to the level of approach. As shown in the figure, there was little drop in removal from 45°F to 60°F approach. At very high approach (130°F), the removal was still 5 to 6% at 2 Ca/S ratio.

The observed effect of the approach to adiabatic saturation (or flue gas humidity) on the SO₂ removal may be due to the positive role of physically adsorbed water on the internal and external surfaces of porous lime particles. The amount of water adsorbed at equilibrium on the lime surfaces increases strongly with increasing humidity (4). Figure 3 shows that the observed SO₂ removals at varying humidities (data from Figure 2) can be correlated nearly linearly with the calculated number of monolayers of adsorbed water (Table 2), based on data from a published study of water vapor equilibrium adsorption on six different hydrated limes as a function of humidity. The study showed that the adsorption per unit lime surface area (or equivalently the number of H₂O layers) was independent of the lime source. For example, the equilibrium amounts of H₂O adsorption on lime are roughly 1.3 and 1.9 monolayers at 50°F and 25°F approaches, respectively. In the steam humidification tests, it is not clear whether the lime rapidly adsorbed water to near the equilibrium level after injection into the flue gas or if the close approach allowed retention of the original surface moisture on the lime. Pilot tests with varying initial lime surface moisture contents can address this question.

The SO_2 removal by lime particles in steam humidified flue gas increased with increasing lime feed rate in almost direct proportion with the Ca/S mol ratio. Thus, the observed sorbent utilization efficiency remained nearly constant with increasing Ca/S. Figure 2 shows that the SO_2 removal at each approach roughly doubled as the Ca/S mol ratio doubled from 1 to 2. These results are consistent with the fact that the increased sorbent loading did not change significantly the environment for sulfur capture for individual sorbent particles. Except for the 10°F approach tests, the differences in the flue gas SO_2 partial pressure were not significant at the two different Ca/S mol ratios because of the relatively low levels of SO_2 removal. In the 10°F approach tests, the SO_2 partial pressure was appreciably lower at the higher Ca/S mol ratio, but this did not affect the performance of individual sorbent particles.

Effect of Water Droplets

Tests with water spray (Coolside) humidification clearly indicate that the presence of liquid water droplets substantially enhances desulfurization performance. Figure 4 shows that at the same final approach to saturation, humidifier SO_2 removals with water spray humidification significantly exceeds that with steam humidification. At 25°F approach and 1 Ca/S ratio, the humidifier removal was 30% with Coolside humidification, as compared with 12% with steam humidification. At 45°F approach, the respective removals were 13% and 6%. The flue gas residence time in the humidifier in Coolside tests was 1.7–2.0 seconds, similar to that in the steam humidification tests. Water was atomized using the Spraying Systems J-12 nozzle with 100 psig atomizing air pressure.

The significant enhancement of the sorbent performance in the presence of evaporating water droplets must result from the wetting of lime particles by water droplets through droplet-particle collisions. This wetting by water droplets would be very efficient in supplying moisture to the lime surfaces and would increase the water content in the lime particles well above that possible by physical adsorption alone.

The humidifier SO_2 removal under conditions of water spraying increased significantly with closer approaches to saturation (Figures 4 and 5). The removal at 1 Ca/S increased from 13% to 31% as the approach decreased from 45°F to 25°F. Above 45°F approach, the removal was less sensitive to the approach.

A lower approach to saturation can enhance SO_2 removal under Coolside humidifying conditions in two ways. First, a higher liquid water feed rate is required at a lower humidifier exit temperature. The theoretical water requirements for cooling to 45°F, 30°F and 25°F approaches in the above runs were 0.288, 0.329, and 0.354 gal/1000 scf flue gas, respectively. The increased water spraying capacity increases the probability of sorbent/droplet interactions. Secondly, the lower approach increases water evaporation time. This allows the wetted lime particles to retain moisture longer on the particle surfaces.

The effect of Ca/S mol ratio observed in the Coolside tests with water droplets present was somewhat different from that observed in steam humidification tests. In the Coolside tests, increasing the lime feed increased humidifier SO_2 removals, but not in direct proportion to the increasing Ca/S ratio (Figure 5). The incremental effect of additional sorbent diminished with increasing Ca/S ratio, particularly at the very close (25°F) approach. Therefore, sorbent utilization efficiency decreased with increasing Ca/S ratio. As shown in Figure 5, humidifier SO_2 removal at 25°F approach was rather insensitive to Ca/S ratio from 1 to 2, increasing from 30 to only 34%. Additional study is required to identify the causes or mechanisms for the

reduced sorbent utilization efficiency with increasing sorbent loading. One possible explanation is that the fraction of the total sorbent particles impacted by the water droplets may be smaller at a higher sorbent particle loading.

Effect of Droplet Size and Evaporation Time

Tests with Coolside humidification with widely varying degrees of water atomization showed that SO_2 removal in the humidifier was higher with larger water droplets and longer droplet drying times at the same final approach to saturation. This result indicates that larger droplets may provide more sorbent-droplet interaction because of either their longer drying times or higher collection efficiencies. The effect of droplet size further confirms the important role of water droplets in the Coolside desulfurization mechanism.

In the Coolside atomization tests, three different nozzles (Spraying Systems J-12, Caldyne 2 mm, and Heat Systems Sonimist 700-3) were tested under widely varying atomizing air pressures and flows. The variation in nozzle type and atomizing pressure produced a wide variation in the drying time in the humidifier (Table 3). The drying time variation resulted primarily from differences in water droplet size distributions produced at different atomizing air pressures, although droplet sizes were not experimentally measured in this study. Humidifier center-line gas temperature profiles were used to estimate drying times in the tests. Figure 6 shows such profiles for the Spraying Systems J-12 nozzle humidifying a 300°F flue gas to 30°F approach at different atomizing air pressures. When enough unevaporated water droplets were present in the flue gas to wet the center-line thermocouples, they read at or close to the adiabatic saturation (wet bulb) temperature. As complete evaporation was approached the thermocouple readings approached the humidifier exit bulk gas (dry bulb) temperature. Thus drying time was estimated from the point at which the profile leveled out at the humidifier exit temperature to within thermocouple error ($\pm 3^\circ\text{F}$). The residence time is based on the plug flow gas velocity at the average humidifier temperature. Based on the temperature profiles, the drying time with the Spraying Systems J-12 nozzle at 30°F approach increased from roughly 0.8 to 2.0 seconds as atomizing air pressure decreased from 115 psig to 45 psig. This reduction in the atomizing air pressure reduced the atomizing air flow through the nozzle. Drying time with the Caldyne nozzle was variable from 0.8–1.2 sec at 30°F by changing the air pressure from 90 to 70 psig (Table 3). The Heat Systems nozzle showed little or no variation in the drying time with air pressure (Figure 7).

Figure 8 shows that the humidifier SO_2 removal with the Spraying Systems J-12 nozzle increased significantly with decreasing atomizing air pressure and increasing drying time. The removal at 30°F approach and 1.5 Ca/S ratio increased from 20% to 28% as atomizing pressure dropped from 115 psig to 55 psig. A similar effect was observed at 45°F approach, the removal increasing from 15 to 19% over 115 to 45 psig air pressures (Table 3). With 0.1 NaOH/Ca(OH)₂ additive injection, the increase was from 34% to 41% from 115 to 55 psig air pressure, at 30°F approach and 1.5 Ca/S ratio.

Using the Caldyne nozzle, the humidifier SO_2 removal at 45°F approach increased from 15% to 25% with decreasing atomizing air pressure from 90 psig to 50 psig. At 30°F approach, there was not as much variation in drying time (Table 3) with air pressure (90–70 psig) and thus less variation in the SO_2 removal (23 to 26%).

The observed SO_2 removal using the Heat Systems nozzle was lower than with the other two nozzles tested, because it produced very small rapidly evaporating droplets, independent of the atomizing air pressure (Figure 7). At 30°F approach

and 1.5 Ca/S, the removals were 19-21%, independent of the atomizing air pressure, as compared with the 20-28% range observed with the other nozzles. At 45°F approach, removals ranged 10-12%, compared with 15-25% observed with the other nozzles.

SO₂ Removal in Baghouse

The baghouse provided significant SO₂ capture in both the steam humidification and Coolside humidification tests. The relative baghouse SO₂ removals, based on the SO₂ content at the baghouse inlet, depended heavily on approach to saturation. In the steam humidification tests, the relative removal at 1 Ca/S increased from 9% to 48% with decreasing approach from 60°F to 10°F. The relative removal also depended on Ca/S ratio, roughly doubling as Ca/S increased from 1 to 2, at lower approaches in the steam humidification tests. The relative baghouse SO₂ removals observed during Coolside testing were about the same or a little less than during steam humidification tests. The total SO₂ removals (across the humidifier and baghouse) were 38% and 21% with Coolside humidification and steam humidification, respectively, at 25°F approach and 1 Ca/S without NaOH (additive) injection. The residence time of solids in the baghouse during the pilot tests ranged 1-2 hours. Because the average solid residence time in the baghouse varied and because some solids dropped out in the baghouse hopper before reaching the bags, observed baghouse removals provide only qualitative desulfurization data.

CONCLUSIONS

Pilot test results with steam and water humidification indicate that the SO₂ capture mechanisms by entrained hydrated lime are highly complex and strongly dependent on the humidification level (approach to adiabatic saturation). Hydrated lime particles have a significant activity and thus provide considerable SO₂ removal in only a few seconds of entrainment in the flue gas under highly humidified flue gas conditions with no water droplets. The adsorbed lime surface moisture may play a key role for the desulfurization reaction based on the strong positive effect of the approach to saturation on SO₂ removal. The presence of evaporating water droplets enhanced the SO₂ removal by the entrained hydrated lime particles significantly. The wetting of lime particles by water droplets may play a key role in the enhanced performance. The beneficial effect of the water was greater at a lower approach to saturation and with larger droplets. The above results indicate that lime injection prior to water spraying, as in the Coolside process, is important for maximum sorbent utilization efficiency and SO₂ removal. Additionally, the sorbent efficiency of the Coolside process may be increased by modifying the lime properties for improved activity under humidified flue gas conditions and by increasing the lime particle-water droplet interactions for enhanced wetting of the particles.

REFERENCES

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2. Yoon, H., Ring, P. A. and Burke, F. P., "Coolside SO₂ Abatement Technology: 1 MW Field Tests", Coal Technology '85 Conference, Pittsburgh, PA, November 12-14, 1985.
3. Yoon, H., Stouffer, M. R., Rosenhoover, W. A., Withum, J. A., and Burke, F. P., "Pilot Process Variable Study of Coolside Desulfurization", AIChE 1987 Spring National Meeting, Houston, Texas, March 1987.

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TABLE 1
CHEMICAL AND PHYSICAL ANALYSES
OF DRAVO LONGVIEW HYDRATED LIME (a)

| Chemical Analyses, wt % | | Particle Size Analyses, wt % | |
|--------------------------------|--------|---|------|
| Moisture | 0.21 | +325 mesh | 21.6 |
| Ash | 75.59 | -325 mesh | 78.4 |
| Carbonate | 1.75 | | |
| Ash Elemental, wt % | | BET Analyses | |
| Na ₂ O | 0.01 | Surface Area, m ² /g 17.3-20.3 | |
| K ₂ O | 0.02 | | |
| CaO | 97.42 | | |
| MgO | 2.25 | | |
| Fe ₂ O ₃ | 0.10 | | |
| TiO ₂ | 0.02 | | |
| P ₂ O ₅ | 0.01 | | |
| SiO ₂ | 0.54 | | |
| Al ₂ O ₃ | 0.57 | | |
| SO ₃ | 0.07 | | |
| Total | 101.01 | | |

(a) Typical analysis of batch used in pilot testing.

TABLE 2
APPROXIMATE EQUILIBRIUM WATER ADSORPTION FOR HYDRATED LIME
BASED ON PUBLISHED DATA (4)

| Approach to Saturation | Water Adsorbed at Equilibrium | |
|------------------------|--|----------------|
| | g H ₂ O/m ² Lime | No. Monolayers |
| 60 | 0.00053 | 1.3 |
| 45 | 0.00059 | 1.5 |
| 30 | 0.00069 | 1.7 |
| 25 | 0.00075 | 1.9 |
| 15 | 0.00087 | 2.2 |
| 10 | 0.00100 | 2.5 |

Based on data at 158°F for six different hydrated limes.

TABLE 3
ATOMIZATION TEST RESULTS

| Nozzle | Approach °F | NaOH/ Ca(OH) ₂ , mass | Atomizing Air | | Estimated Drying Time, sec | Humidifier SO ₂ Removal % |
|-----------------------|----------------|--|---------------|------------------------------|----------------------------------|--|
| | | | psig | scf/ gal H ₂ O | | |
| Spraying Systems J-12 | 45 | 0 | 115 | 78 | 0.5-0.7 | 15 (15) |
| | 45 | 0 | 100 | 69 | 0.9-1.1 | 15 (14) |
| | 45 | 0 | 85 | 57 | - | 17 (16) |
| | 45 | 0 | 70 | 51 | 1.1-1.5 | 17 (18) |
| | 45 | 0 | 55 | 44 | 1.5-1.9 | 19 |
| | 45 | 0 | 45 | 38 | 1.7-1.9 | 19 |
| | 30 | 0 | 115 | 74 | 0.7-0.8 | 20 (20) |
| | 30 | 0 | 100 | 63 | 0.8 | 23 |
| | 30 | 0 | 85 | 56 | 1.0 | 24 (24) |
| | 30 | 0 | 70 | 46 | 1.9-2.1 | 27 |
| | 30 | 0 | 55 | 40 | 1.9-2.1 | 28 |
| | 30 | 0.1 | 115 | 62 | 0.7-0.8 | 34 (36) |
| | 30 | 0.1 | 100 | 54 | 0.8 | 39 |
| | 30 | 0.1 | 85 | 47 | 1.0 | 41 |
| | 30 | 0.1 | 70 | 39 | 1.9-2.1 | 40 (41) |
| | 30 | 0.1 | 55 | 34 | 1.9-2.1 | 41 |
| Caldyne | 30 | 0 | 90 | 131 | 0.8 | 23 (23) |
| | 30 | 0 | 80 | 119 | 0.9-1.1 | 24 (26) |
| | 30 | 0 | 70 | 101 | 1.0-1.4 | 26 |
| | 45 | 0 | 90 | 159 | 0.5-0.8 | 15 (14) |
| | 45 | 0 | 80 | 139 | 0.7-0.7 | 18 |
| | 45 | 0 | 60 | 108 | 1.0-1.2 | 21 (20) |
| | 45 | 0 | 50 | 92 | 1.5-1.8 | 25 |
| | 45 | 0 | 45 | 81 | 1.9-2.1 | 27 |
| Heat Systems | 45 | 0 | 70 | --- | 0.6-0.8 | 10 |
| | 45 | 0 | 60 | 295 | 0.6-0.8 | 10 |
| | 45 | 0 | 55 | 273 | 0.6-0.8 | 11 (12) |
| | 45 | 0 | 45 | 213 | 0.6-0.8 | -- |
| | 30 | 0 | 70 | --- | 0.7-0.8 | 19 |
| | 30 | 0 | 60 | 271 | 0.7-0.8 | 19 |
| | 30 | 0 | 55 | 260 | 0.7-0.8 | 21 |
| | 30 | 0 | 45 | 212 | 0.7-0.8 | 23 |
| | 30 | 0 | 40 | 191 | 0.9-1.1 | 24 |
| | 30 | 0 | 35 | 171 | 1.1-1.5 | 25 |

Numbers in parentheses are repeat tests.

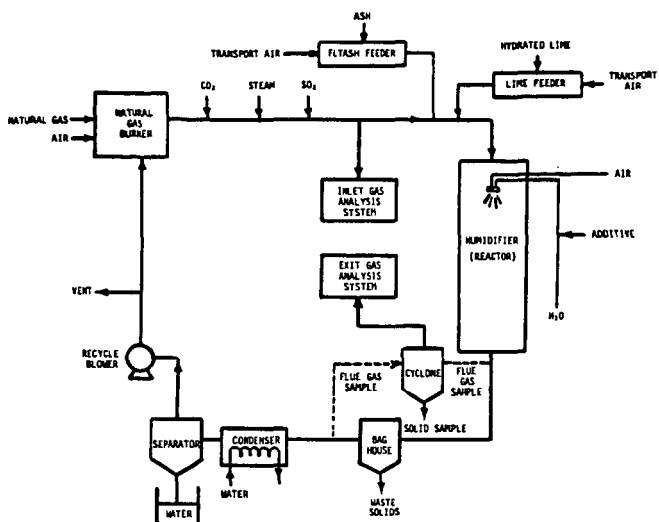


Figure 1. Schematic of Pilot Unit.

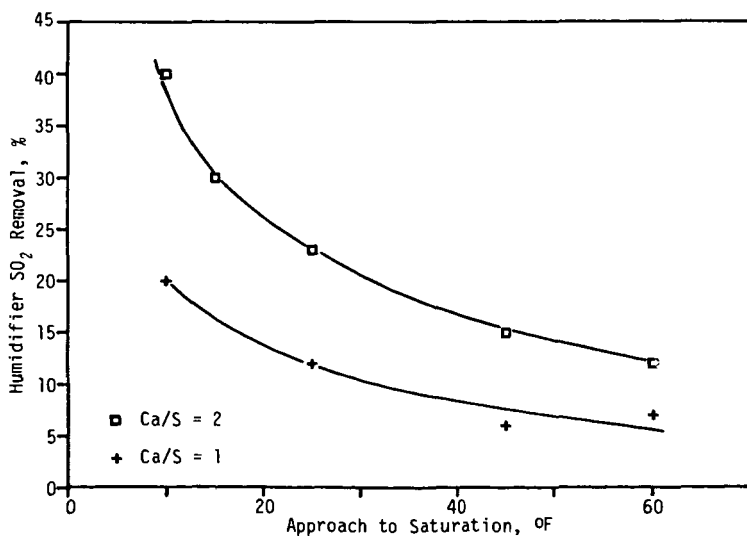


Figure 2. Steam Humidification Tests. Humidifier Removal: 2 sec residence time, 1500 ppm SO₂.

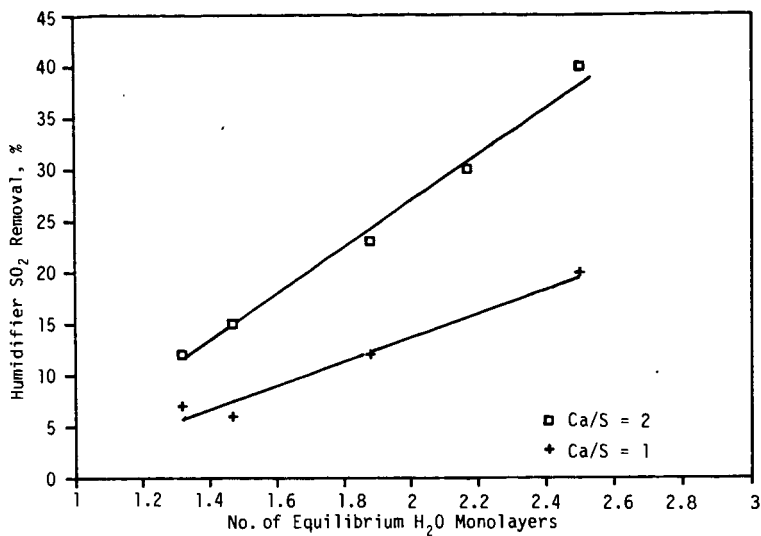


Figure 3. Steam Humidification Tests. Humidifier Removal: 2 sec, 1500 ppm SO₂.

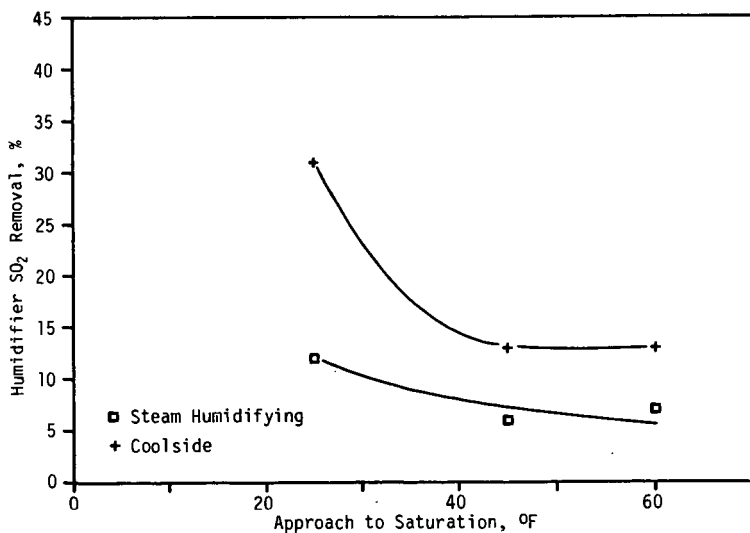


Figure 4. Comparison of Coolside Process and Steam Humidification Test Results. 1 Ca/S, 0 NaOH, 1500 ppm SO₂.

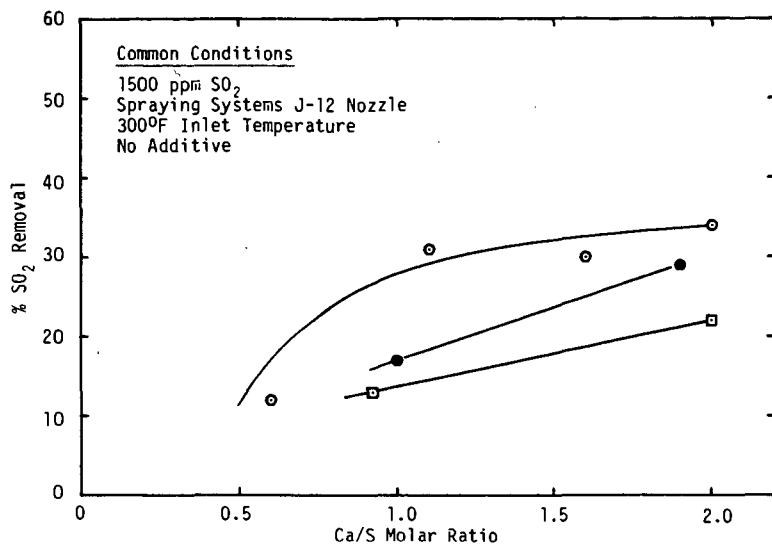


Figure 5. Effect of Ca/S Ratio and Approach on Humidifier SO_2 Removal in Coolside Humidification Tests. \circ 25°F \bullet 30°F \square 48°F Approach.

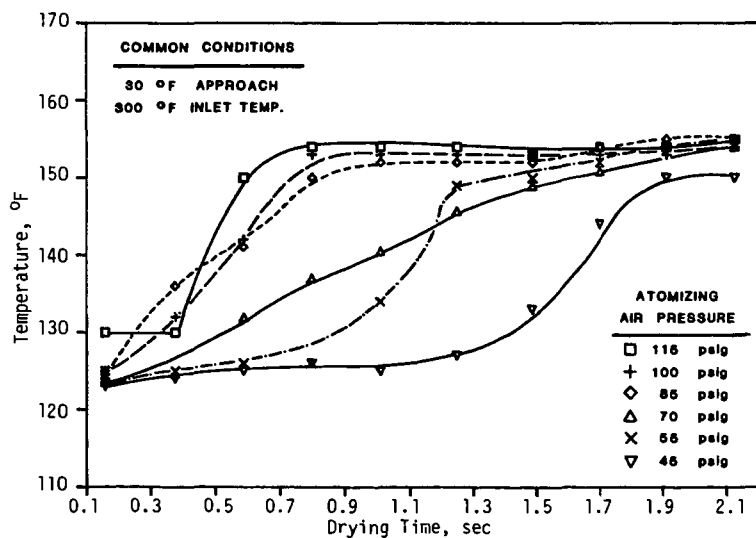


Figure 6. Humidifier Temperature Profile. Spraying Systems J-12 Nozzle.

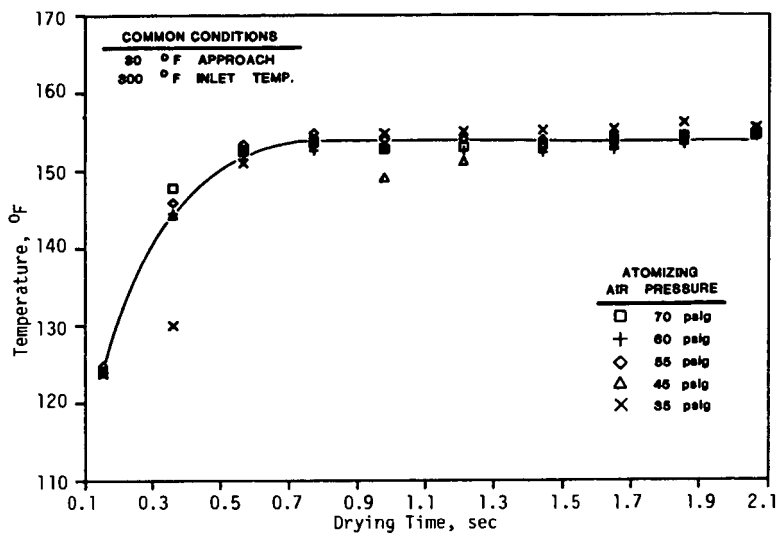


Figure 7. Humidifier Temperature Profile. Heat Systems 700-3 Nozzle.

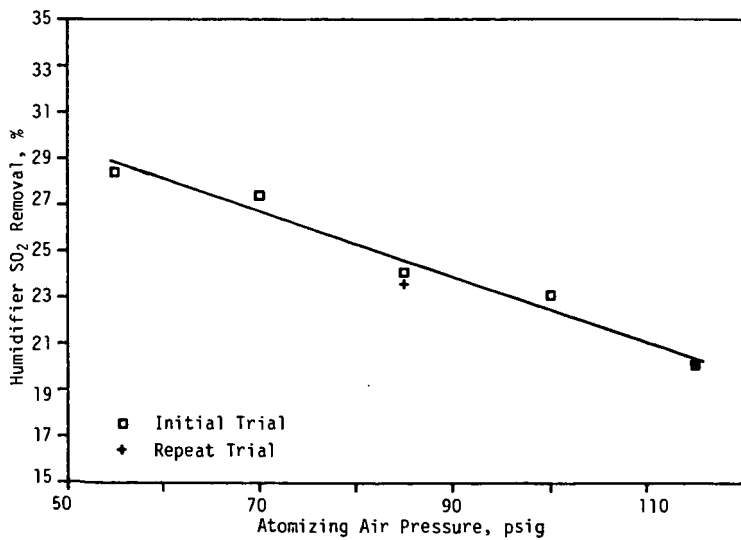


Figure 8. Effect of Atomization on SO₂ Removal. Spraying Systems J-12 Nozzle.